INTERDEPARTMENTAL CORRESPONDENCE

GOODYEAR ATOMIC CORPORATION

TO: D. H. Francis
General Manager
DEPT: 101
LOCATION: X-100

DATE: March 18, 1959
FROM DEPT: 534
CODE NO: GAT-534-59-73
REFERENCE:

SUBJECT: Report of Investigation of Violent Chemical Reaction in F_2 Surge Drum, X-344, on March 4, 1959.

DISTRIBUTION:

W. A. Brown
D. W. Doner
M. L. Geneva
M. R. Hertz
C. R. Milone
J. B. Mitchelson
W. F. Culp
L. T. Oyler
W. M. Poor
G. H. Reynolds
R. B. Stambaugh
W. H. Taylor
B. W. Penland

The Investigation Committee, appointed by D. H. Francis on March 5, 1959, (Ltr. D. H. Francis to G. H. Reynolds, et al., Subject: "Committee to Investigate Violent Chemical Reaction in F_2 Surge Drum, X-344, March 4, 1959"), was comprised of the following:

M. R. Hertz, Chairman
M. L. Geneva
W. M. Poor
J. H. Dalton

J. H. Dalton terminated during the investigation and was replaced with L. T. Oyler.

The attached report represents the findings of the Committee.

M. R. Hertz, Chairman

MRH:mm

Attach.

INTERDEPARTMENTAL CORRESPONDENCE
GOODYEAR ATOMIC CORPORATION

TO: G. H. Reynolds
W. A. Brown
C. R. Milone
D. W. Doner
M. L. Geneva
W. M. Poor
M. R. Hertz
J. H. Dalton

DATE: March 5, 1959

SUBJECT: COMMITTEE TO INVESTIGATE VIOLENT CHEMICAL REACTION IN F_2 SURGE DRUM, X-3144, MARCH 4, 1959

The following committee is appointed to investigate the violent chemical reaction that occurred in FE 620, F_2 surge drum on the morning of March 4, 1959:

M. R. Hertz, Chairman
M. L. Geneva
W. M. Poor
J. H. Dalton

It is requested that the above committee investigate the incident and report their findings for internal distribution. At the present time, this incident is not reportable under the AEC criteria. Should substantial damage be revealed during the investigation it will be necessary to reconsider the classification of this incident.

A report of this incident should be completed by March 18, 1959.

D. H. Francis
General Manager

DHF:jrf

REPORT OF INVESTIGATION OF VIOLENT CHEMICAL REACTION IN F_2 SURGE DRUM, X-344 ON MARCH 4, 1959.

1. DESCRIPTION OF SYSTEM INVOLVED IN THE REACTIONS.

A simplified schematic diagram of the portion of the system actually valved in at the time of the explosion is shown in Figure 1. A more complete schematic of the entire system is available in Dwg. 820 M 90. Fluorine produced in the cell room flows through the surge tank, a mist filter, and a five-stage centrifugal fluorine compressor to the inlet of the HF condensing system, which consists of three heat exchangers in series. The first, HFE 662, is a gas-to-gas cooler in which heat in the inlet gas is transferred to the cold fluorine leaving the system. The partially cooled inlet gas proceeds to the second heat exchanger, HFE 663, where it is cooled to -60°F by a Freon-114 "brine" loop, and thence into the third exchanger where it is cooled to -120°F by a second F-114 brine loop. The outlet fluorine is metered by a flow orifice and the outlet pressure to the tower area controlled by a DBM and control valve. The HF content of the fluorine from the cells is about 15 percent; after passing through the condensers it contains about two percent. The condensed HF drains from the heat exchangers to a HF "run-down" tank, HFE 666A, from which it is periodically transferred to the HF storage tanks by nitrogen pressure. The HF run-down tank is equipped with load cells which indicate on a weight recorder in the control room.

Fluorine and hydrogen pressures and the fluorine-hydrogen pressure differential are controlled by DBM's and PRC's on the fluorine and hydrogen surge drums. These instruments operate control valves in the fluorine and hydrogen compressor suction lines to maintain surge drum pressures at approximately atmospheric. Fluorine pressure beyond the compressor is about 1.5 psig. Normal fluorine temperature leaving the cells is 180-190°F. It is cooled in exposed piping to a few degrees above ambient at the surge drum, heated by the compressor considerably above ambient, and leaves the condensers about ambient. In addition to the above the plant is protected from excursions by the "Q" circuit which is activated when the pressure differential between the hydrogen and fluorine surge drums exceeds 3 inches of water. This instantly shuts off the fluorine cell rectifiers, opens the fluorine surge drum to vent, shuts off the fluorine and hydrogen compressors, closes a block valve in the fluorine line to the fluorination towers and stops the powder feed screws on the towers.

2. CHRONOLOGY (OBTAINED FROM OPERATING PERSONNEL, OPERATION LOG AND RECORDER CHARTS).

0012 - Initial start-up of fluorine plant. Forty cells were on the line at 2000 amperes.

0012-0050 - Continuous attempts were made to get two different fluorination towers to fire. Continuous firing was not obtained although there were indications on tower temperature charts that some reaction took place sporadically.

Fluorine preheaters at tower inlets were operating properly. This situation had occurred once before and it was found that a nitrogen purge had been left on in the fluorine system, diluting the fluorine sufficiently that the towers would not fire. Dilution of the fluorine was also suspected because the fluorine flow orifice indicated a rate somewhat larger than normal for 40 cells at 2000 amperes. Accordingly, a fluorine sample was obtained at about 0050 at the tower inlet for analysis.

0055 - The feed plant laboratory reported the fluorine content of the sample as 39.12 percent.

0055-0105 - A search was made for open nitrogen purge valves. About 0100 Mr. Norman, the Shift Foreman, checked the HF condenser room and detected the odor of hot insulation, but did not attach any significance to this at the time. Just before 0105, personnel checking the cell rooms noticed a rise in fluorine pressure on the individual PI's at the cells.

0105 - The control room operator observed the pressure increase in the F_2 system and shut down the fluorine cell rectifiers. The fluorine compressor was left running in hopes that the excess gas would be exhausted through the towers and cold traps.

0106 - The "Q" circuit shut down the rest of the plant when the F_2-H_2 differential pressure reached 3 inches of water. The shut-down included stopping the F_2 compressor, opening the vent valve at the F_2 surge drum, and closing the block valve in the main F_2 line to fluorination towers.

0107 - Mr. Norman observed that the weight recorded on the HF run-down tank had increased in less than 5 minutes from about 500 pounds to off scale (above 1200 pounds). Normal rate of condensation of HF would be about 10-15 pounds per hour at 2000 amperes.

0106-0117 - Pressure in the F_2 system was off scale on all instruments. All manual vent valves were opened in an attempt to relieve the pressure. The main vent stack pressure was off scale (5 inches of water) indicating that the vent system was unable to handle the volume of gas being produced in the system. The hydrogen system pressure also went off scale and the manual vents were opened. Overpressure in this system must have resulted from gas being forced under the fluorine cell skirts against the hydrostatic pressure of the electrolyte. This requires about 12 inches of water differential.

0117 - A violent chemical reaction was heard by all personnel in the building. No personnel were on the second floor at the time. To all operating personnel on the first floor it seemed that the reaction had taken place in an adjacent room.

A quick inspection of the plant was made. Broken concrete grouting was noticed at the base of the F_2 surge drum. A fluorine fire was discovered at one fluorine cell outlet flange gasket. Electrolyte had blown out of the sampling valves of several fluorine cells.

0117 - Approximately 0150 - Pressure remained off scale in the entire system. Additional checks were made and all vent valves were open. Pressures finally dropped back to atmospheric at about 0150. At this time an attempt was made to isolate HFE 663A cooler from the Freon brine system, but while trying to remove the cap from the outlet block valve, the bonnet was accidentally screwed out of the valve body, releasing Freon-114. The -60°F brine loop was blocked farther back, but Freon-114 leaked into the atmosphere at the loose bonnet for about one-half hour followed by HF. About this time the contents of the HF run-down tank were blown into empty HF storage tank "A". The run-down tank was then valved back to the condensers and again collected several hundred pounds of liquid Freon-114.

The refrigeration operator had observed a temperature rise in the -60°F brine system during the start-up. He had been unable to account for it since the brine level was satisfactory, the loop pressure was holding at the set value (125 psi), the brine circulation pumps were operating, and the Freon-22 refrigeration system was operating properly.

Immediately following assignment, the Investigation Committee met with feed plant technical personnel. After a brief review of the incident, the Committee requested that gas samples be obtained for analysis of reaction products, after which operating personnel were free to proceed with the process of preparing plant for operation. It was recommended that all parts of the F_2 system which could possibly contain Freon-114 be purged and checked by gas analysis and that parts of the brine loop suspected of being contaminated with HF be purged and checked by analysis before refilling with Freon.

3. SURVEY OF DAMAGE.

a) The Mechanical Inspection Department inspected the F_2 surge drum and determined that the vessel was undamaged.

b) In addition to one gasket fire at a cell outlet flange many cells had lowered electrolyte levels, leaking flange gaskets, and plugged HF feed dip legs. There was no detectable mechanical damage to the F_2 cells. All cell room hydrogen headers and valves in use contained electrolyte.

c) The rupture disk on the vent line of HF run-down tank HFE 666A had ruptured outward from the tank. The vent lines from all three run-down tanks are connected to a common vent system which overpressured. This pressure ruptured the disk on HF run-down tank HFE 666B from the vent toward the tank. These rupture disks are rated at 60 psi.

d) HF Cooler HFE 663A, which had obviously developed a major Freon leak, was removed and cut open for inspection. About four feet of the monel shell, near the F_2 inlet, had been hot enough to discolor and was slightly warped. The tube bundle was beyond economical repair. The copper spacers and monel tube supports were partially melted and copper Freon tubes were ruptured.

The original leak which furnished Freon for the fire appeared to have occurred where one of the tubes passed through a monel spacer sheet. At this point, the tube had a groove eroded or corroded all the way around it together with an enlarged hole in the monel sheet. With the exception of this one point the tubes appeared to have suffered little corrosion and had maintained essentially full wall thickness. The failed bundle was submitted to the Metallurgy Department for full analysis of the damage.

e) Since an extremely high velocity, hot jet of gas must have impinged on the tube bundle of the -120°F Condenser, HFE 664A, this item was removed, cut open, and inspected even though it had passed a gas pressure test at 100 psi. No damage was found.

4. RESULTS OF GAS SAMPLE ANALYSIS.

Samples were taken from the F_2 surge drum and from the gas in the product cold traps. Results of mass spectrometer analyses are shown below.

Compound	F_2 Surge Drum	Roughing Trap C	Clean-up Trap F	Clean-up Trap H	Roughing Trap A	Clean-up Trap E
HF		Trace	Trace	Trace	0.2	0.3
N_2	4.7	57.0	57.0	63.3	49.2	67.6
O_2	0.2	15.9	15.0	16.8	14.9	10.1
A		0.5	0.5	0.1	0.5	0.4
CO_2		Trace	Trace	Trace	$<$0.1	Trace
F_2		1.7	8.3	0.5	1.1	0.4
CF_4		13.5	7.8	12.8	15.8	4.1
Cl_2		4.8	3.2	3.7	5.3	1.5
ClO_2F			0.1			
Freon-13		2.6	0.3	2.1	2.8	0.3
Freon-114	95.1	0.1	0.1	0.2	$<$0.1	---
Freon-115		0.2	0.1	0.2	0.5	0.5
UF_6		3.7	6.8	----	9.7	14.8

The reaction products of Freon-114 and fluorine, Cl_2, CF_4 and Freon-13, were found in the product traps. The product traps were blocked off from the F_2 system a few minutes before the violent reaction. This shows that a reaction had been taking place in the system for some time.

5. DISCUSSION.

A logical sequence of events can be reconstructed from the data collected.

a) A leak in HF Condenser HFE 663A existed from some time either before start-up or immediately after start-up at 0012. Liquid Freon-114 spraying from this leak under 125 psi ignited and burned in fluorine. This is shown by the fact that a temperature rise was noted in the Freon brine system from start-up, that the fluorine was too dilute to ignite the towers, and that Freon 114-F_2 reaction products were found in the cold trap system, which had been isolated about 10 minutes before the violent reaction.

b) At about 0105 other Freon tubes in HFE 663A, heated nearly to the melting point by the fire in the condenser shell, ruptured. This flooded the condenser system with liquid Freon, which flashed to vapor at an initially semi-explosive rate as it struck several square feet of semi-molten metal, producing a pressure surge which shut off the plant through the "Q" circuit. At this time, the HF run-down tank, HFE 666A, flooded with liquid Freon.

c) Liquid Freon vaporized at a rate too great to be handled by the vent system, and the vapor traveled back to the F_2 surge drum where it mixed with a large volume of fluorine, producing a violent chemical reaction. The resultant pressure surge forced large quantities of gas under the F_2-H_2 separator skirts in the fluorine cells, forced electrolyte into the hydrogen header and out some sampling valves and plugged HF feed lines to individual cells. In addition, it blew out a Teflon flange gasket at the cell-header connection of one cell, producing a minor fluorine fire.

6. REACTION OF FREON-114 WITH FLUORINE.

a) Reaction mechanism is discussed fully by F. E. Massoth in AEC Report, GAT-234, "Reactions of Freon-114 with Fluorine". From thermodynamic calculations it was determined that the reaction energy is approximately 300 Kg. Cal. per mol, which is considerably larger than that for F_2 with UF_4. It appears that sufficient heat would certainly be available to produce the effects found in Cooler HFE 663A.

b) R. H. Capps and E. J. Barber reported in AEC Report, K-1196, that they were able to initiate explosions with an electric spark in Freon-114-F_2 gas mixtures over a large range of compositions. Explosions were obtained with 13 percent to 85 percent Freon-114 in fluorine. The tests were run at a total pressure somewhat less than atmospheric and at approximately room temperature.

c) Explosion test work of Department 534 has indicated that detonation may occur spontaneously over a wide range of temperatures and pressures in a mixture of F_2 with any compound containing a carbon-carbon bond. Freon-114 has not been tested but violent reactions have been obtained with MFL oil and C-816 (perfluorodimethylcyclohexane), both fully fluorinated compounds which would be expected to be less reactive than Freon-114.

7. DESCRIPTION OF SECOND VIOLENT REACTION OCCURRING IN F_2 SURGE DRUM AT 1555, MARCH 6, 1959.

By noon on March 6, all equipment except the "A" HF condensing system had been repaired and purged, and the plant was restarted using the "B" HF condensing system. Start-up was normal and the plant had been operating at full capacity for about two hours when a violent reaction occurred in the F_2 surge drum. The partially cured base grouting on the drum was shattered as before. Some electrolyte was thrown out of the sampling valves on a few fluorine cells and some HF feed lines were plugged but the effects were not nearly as severe. There was no temperature rise in the HF condensing system. Pressure in the system showed no increase before the reaction and returned to normal immediately afterward, although the plant was shut down by the "Q" circuit. Gas samples were obtained from the F_2 surge drum and HF condenser outlet immediately after the reaction. The surge drum sample contained about 90 percent air, 2.3 percent Cl_2, 3.4 percent CF_4, and 3.5 percent F_2. The HF condenser sample contained about 10 percent air, 80 percent fluorine, 0.8 percent Cl_2, 2.6 percent CF_4, 0.2 percent Freon-13, 1.3 percent Freon-114 and traces of ClF and ClO_2F. It was immediately obvious that the second reaction was due to Freon-114 left in the system from the previous reaction. Also, since the previously air purged surge drum still contained 90 percent air after four hours of operation, purging procedures should be followed carefully with analysis.

The system was purged with nitrogen using mass spectrometer analysis to follow the progress. The plant was restarted at about 0100 March 7, with no further difficulty to date. Periodic samples were taken from the fluorine system at the HF condenser outlet, through March 7 and March 9. (The plant was scheduled down March 8.). Traces of Freon-114 were found through March 7, disappearing on March 9.

7. MONETARY LOSS.

Estimated direct labor and material charges resulting from the two violent reactions will total $8700.00. Final exact charges are not available at this date.

8. RECOMMENDATIONS.

a) That the possibility of continuously monitoring the Freon content of the fluorine from the HF condensing system, using either existing or additional instrumentation, be investigated.

b) Until recommendation (a) is activated, a sample from the fluorine system should be analyzed for Freon before each plant start-up following a shut-down of more than one day duration.

c) That at plant start-ups and once a shift thereafter, the exact time should be marked on all recorder charts. If charts are not synchronized it is difficult to establish sequence of operation.

d) That a positive method be used to secure all Freon valve bonnets.

e) That all fluorine cell electrolyte sample valves be kept fully closed when not in use.

INVESTIGATION COMMITTEE

M. R. Hertz
Department 534

L. T. Oyler
Department 252

M. L. Geneva
Department 820

W. M. Poor
Department 731

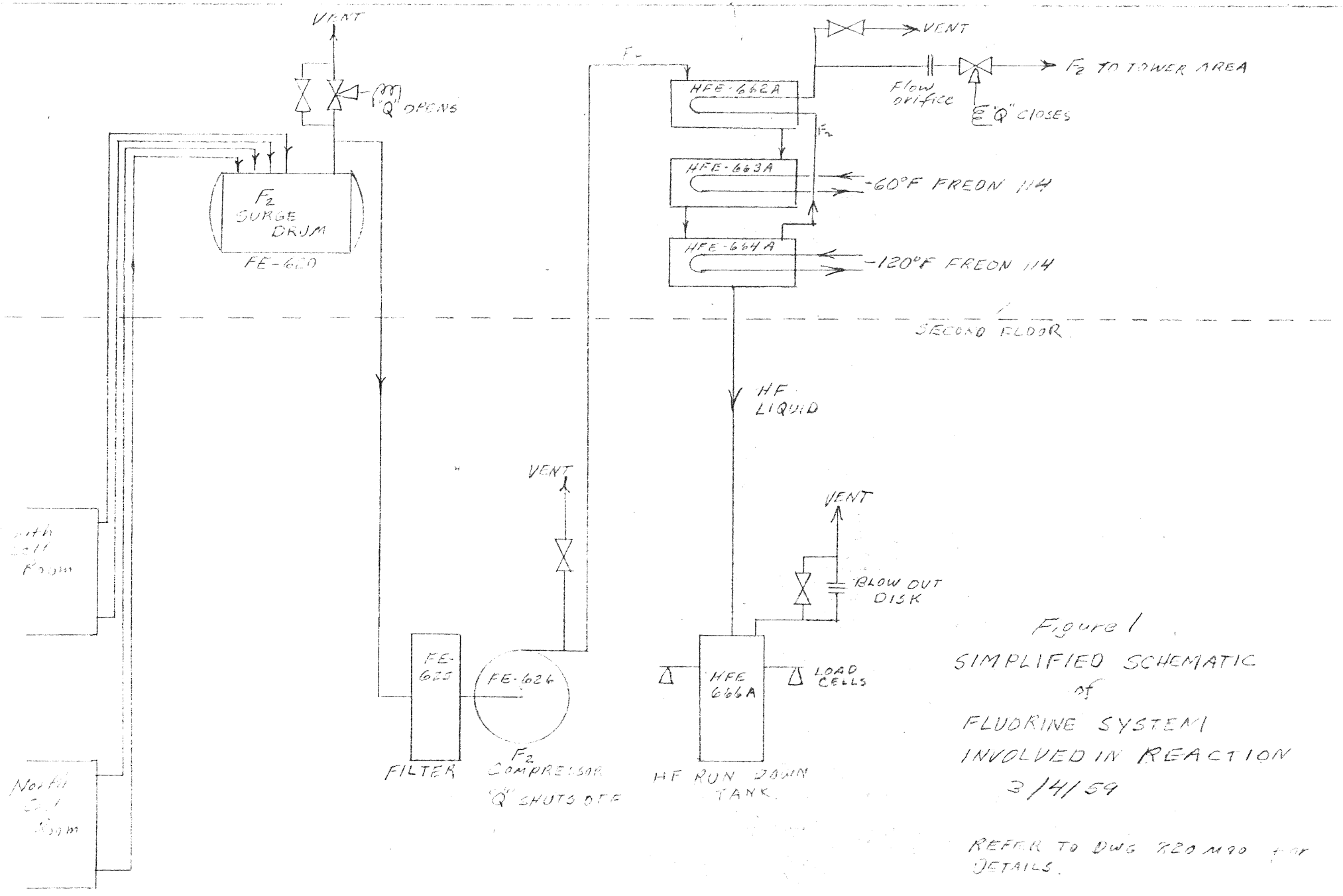


Figure 1

SIMPLIFIED SCHEMATIC

of

FLUORINE SYSTEM

INVOLVED IN REACTION

3/14/59

REFER TO DWG K20 M90 for DETAILS.

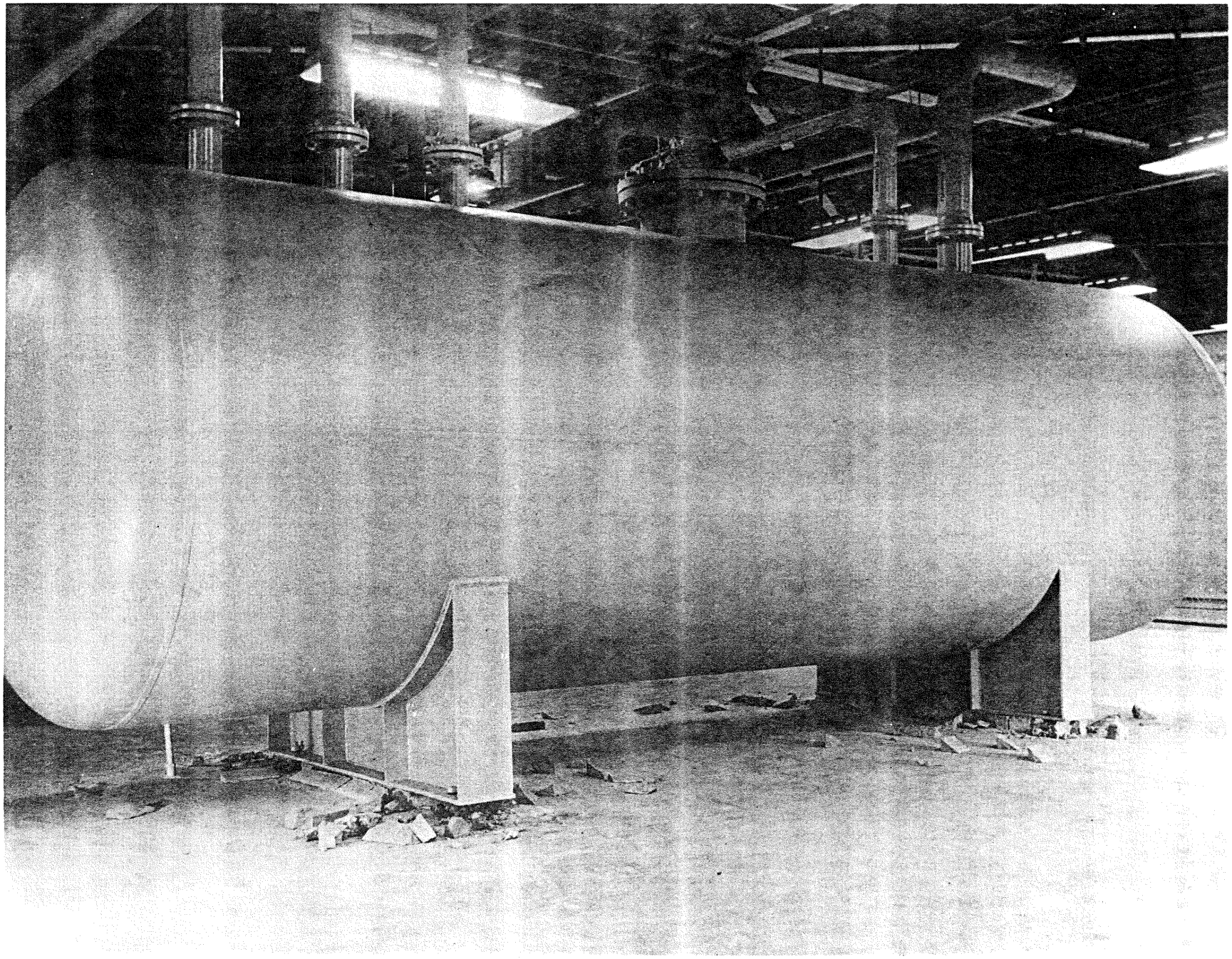


Fig. No. 3 "Fluorine surge drum showing shattered base grouting."

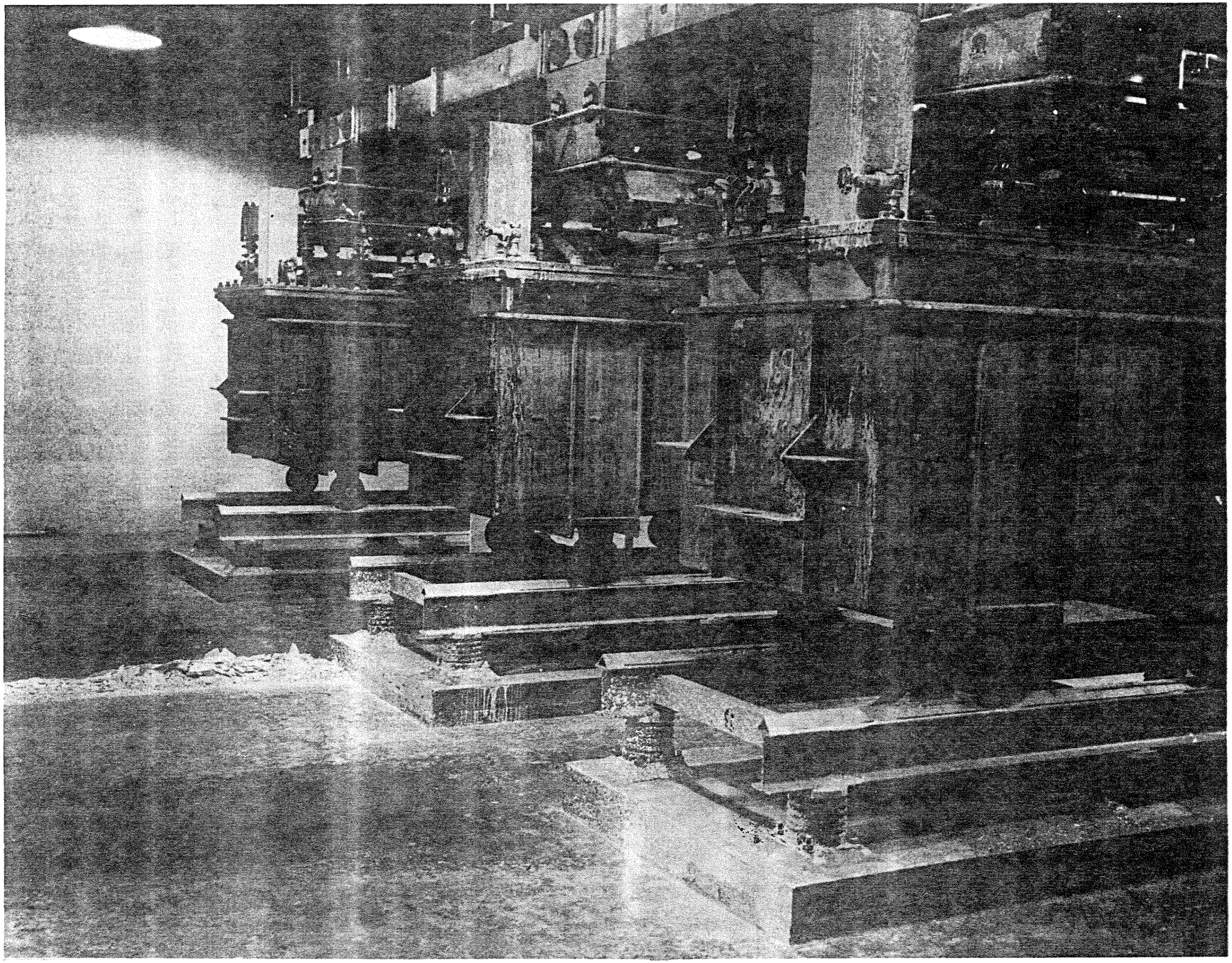


Fig. No. 4 "South fluorine generation room showing spilled electrolyte from sampling valves."

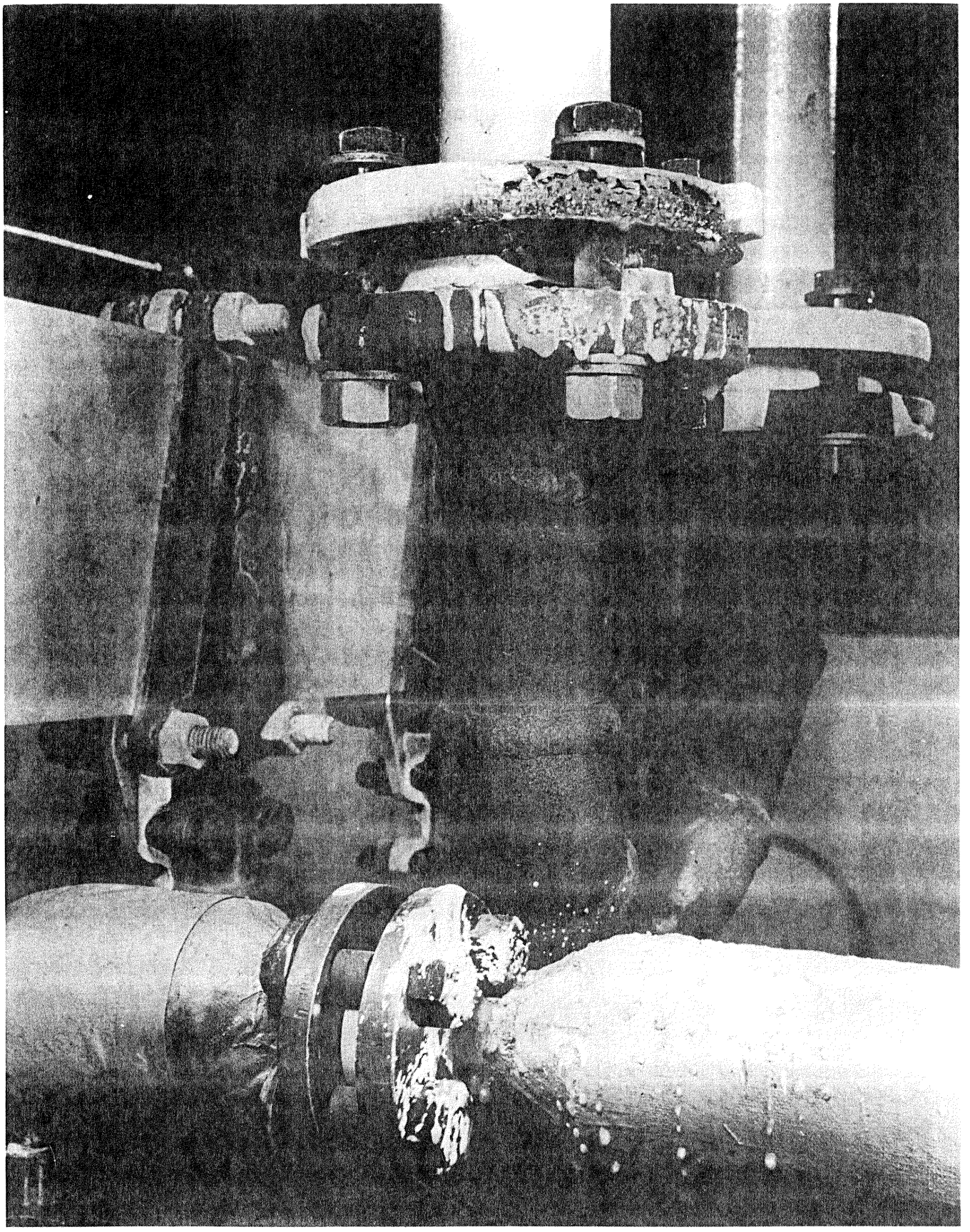


Fig. No. 5 "Fluorine cell outlet flange where fire occurred."

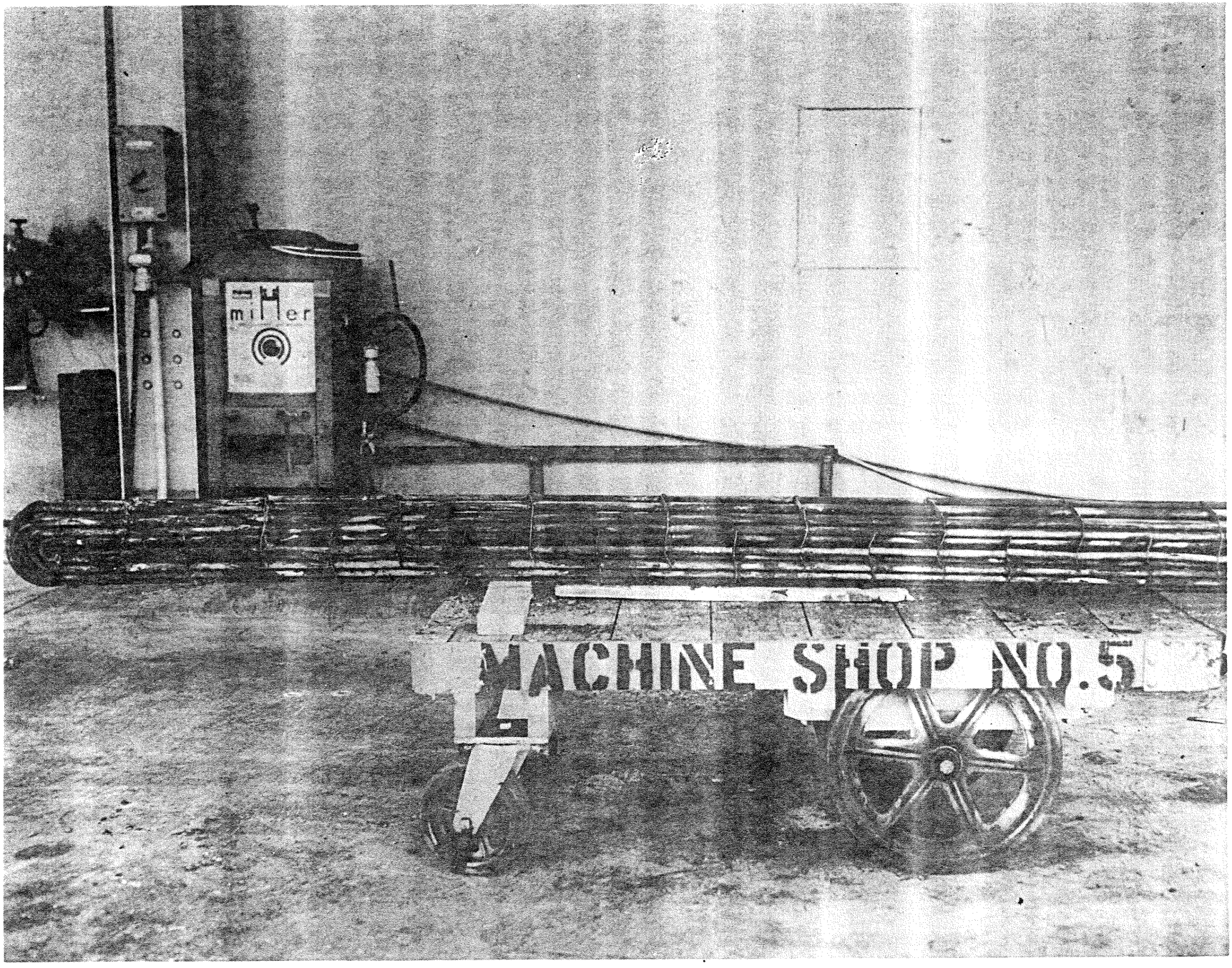


Fig. No. 6 "Tube bundle from gas cooler HFE663A."

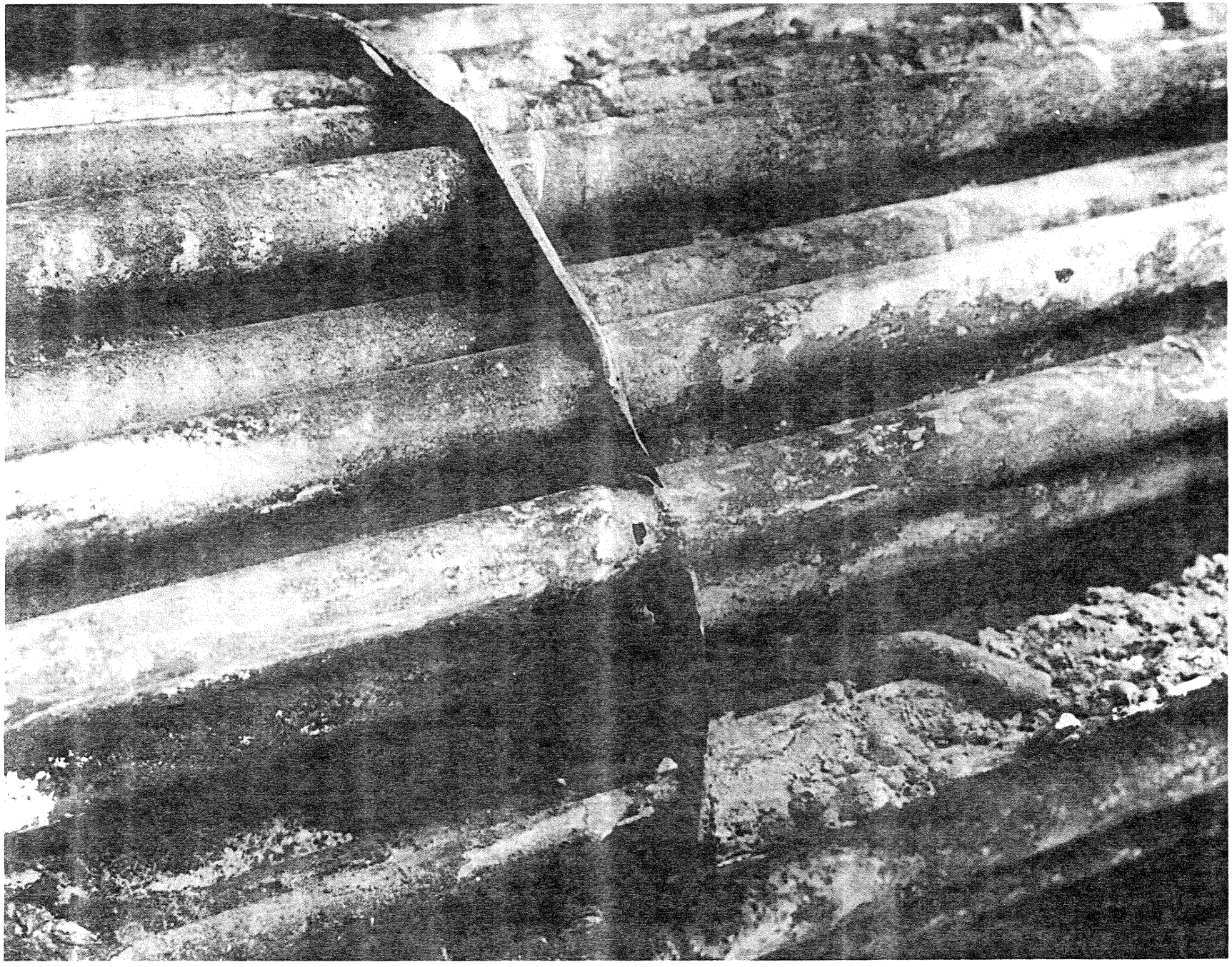


Fig. No. 7 "Necked down tube in gas cooler HFE663A. This may be the point of the original freon leak."

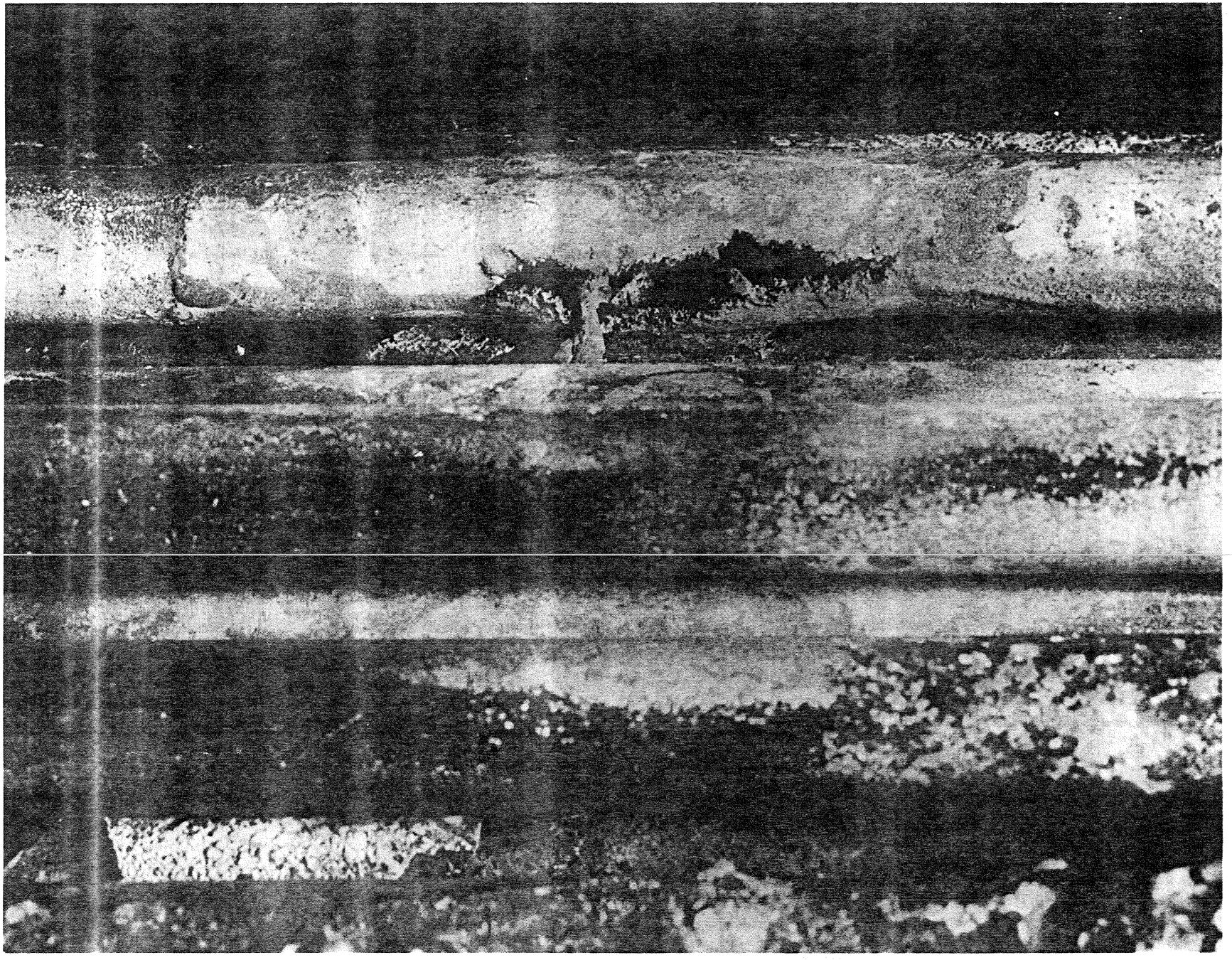


Fig. No. 8 "Ruptured freon tube in gas cooler HFE663A."

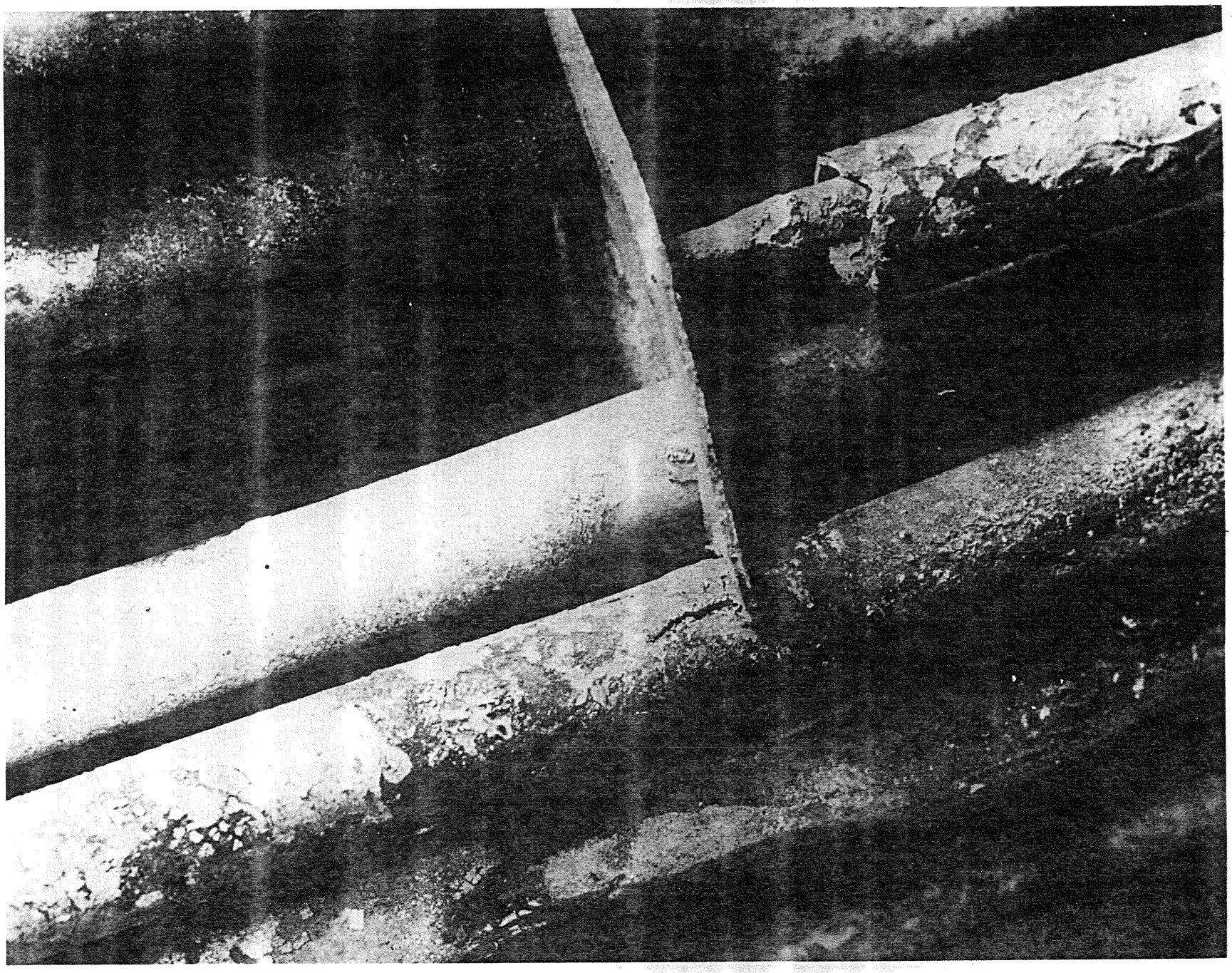
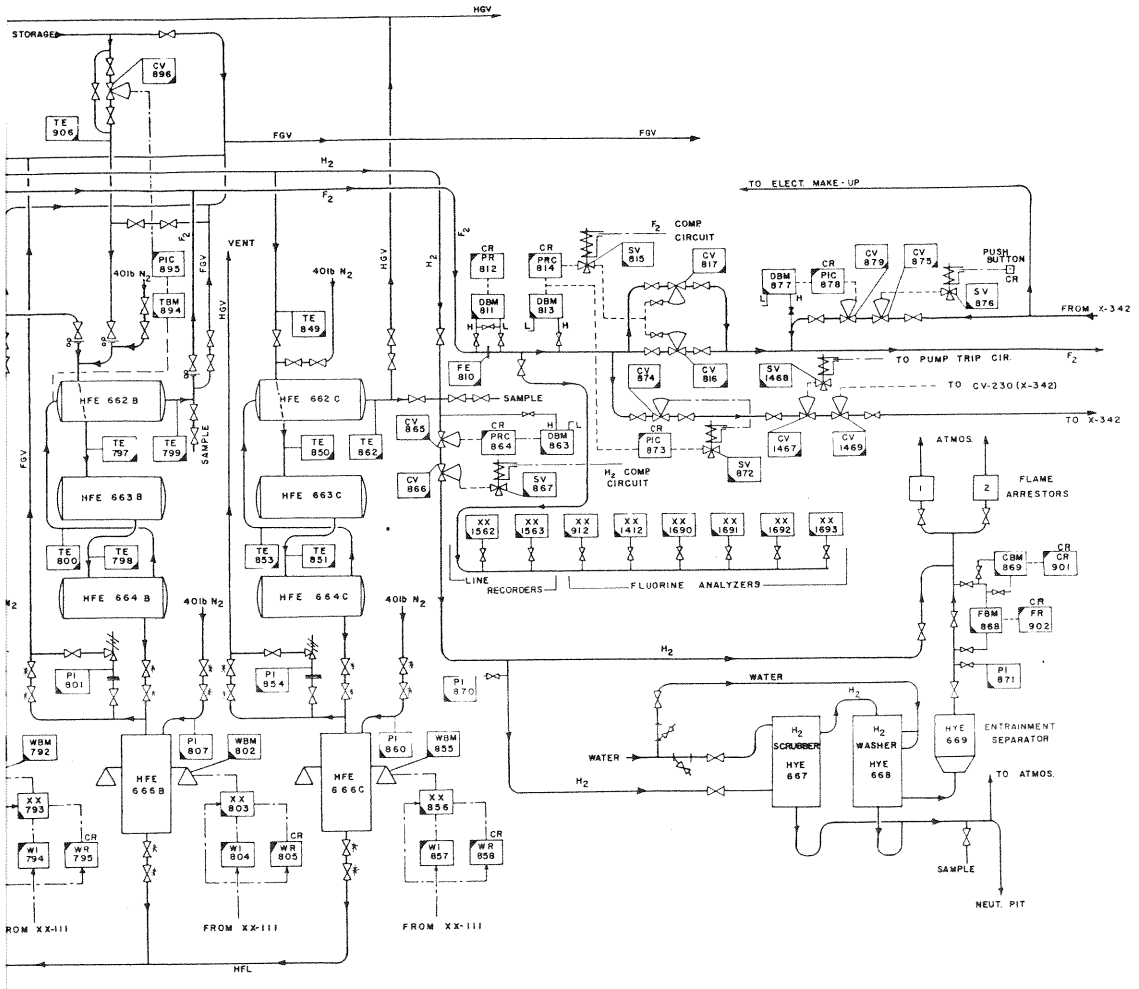


Fig. No. 9 "Melted tube spacers and ruptured tubes in gas cooler HFE663A."



VALVES WITH EXTENSIONS

INSTRUMENT LEGEND

DRAWN BY EMM	6-12-57	INSTRUMENTATION APPLICATION	820 M 90
CHECKED BY EMT	6-12-57	X-344 FLUORINE GENERATION SHEET 2	